CHEMISTRY 273

TRANSFORMATION OF QM OPERATOR MATRICES WITH CHANGE OF BASIS SET

1. We have defined matrices for quantum mechanical operators with respect to a basis set, *e.g.*,

$$(\underline{\underline{\mathbf{H}}})_{ij} = \langle \chi_i | \hat{H} | \chi_j \rangle$$

or

$$(\underline{\underline{\mathbf{S}}})_{ij} = \langle \chi_i | \chi_j \rangle$$

2. How does a matrix for an operator (e.g., $\underline{\underline{\mathbf{H}}}$ or $\underline{\underline{\mathbf{S}}}$) change if there is a new basis which is a linear combination of the original:

$$\underset{\text{new}}{\underset{\uparrow}{\chi'_i}} = \sum c_{ki} \underset{\text{old}}{\underset{\uparrow}{\chi_k}} \qquad \qquad \underline{\underline{\mathbf{H}}} \rightarrow \underline{\underline{\mathbf{H}'}} \qquad \underline{\underline{\mathbf{S}}} \rightarrow \underline{\underline{\mathbf{S}'}}$$

3. Here's how!

$$(\underline{\underline{H'}})_{ij} = \langle \chi'_i | \hat{H} | \chi'_{ij} \rangle$$

$$= \left\langle \sum_k c_{ki} \chi_k \middle| \hat{H} \middle| \sum_\ell c_{\ell j} \chi_\ell \right\rangle$$

$$(\underline{\underline{H'}})_{ij} = \sum_k \sum_\ell c^*_{ki} c_{\ell j} \left\langle \chi_k \middle| \hat{H} \middle| \chi_\ell \right\rangle$$

$$\underline{\underline{H'}}_{ij} = \sum_k \sum_\ell \tilde{c}^*_{ik} H_{k\ell} c_{\ell j}$$

$$\underline{\underline{\mathbf{H}'}} = \underline{\underline{\tilde{\mathbf{C}}}} * \underline{\underline{\mathbf{H}}}\ \underline{\underline{\mathbf{C}}}$$

and similarly

$$\underline{\underline{\mathbf{S}'}} = \underline{\underline{\tilde{\mathbf{C}}}} * \underline{\underline{\mathbf{S}}}\ \underline{\underline{\mathbf{C}}}.$$

4. Thus if

$$\underline{\chi}\ \underline{\underline{C}} = \underline{\chi}' = (\chi_1' \ \ \chi_2' \cdots \chi_N')$$

then

$$\underline{\underline{\tilde{C}}}^* \underline{\underline{H}}\ \underline{\underline{C}} = \underline{\underline{H}}'$$

$$\underline{\underline{\tilde{C}}}^* \underline{\underline{S}}\ \underline{\underline{C}} = \underline{\underline{S}}'$$

5. An example of a change of basis set is a transformation from a.o.'s to m.o.'s:

$$(|\phi_1\rangle\ |\phi_2\rangle\ |\phi_3\rangle \cdots |\phi_N\rangle) = (|\chi_1\rangle\ |\chi_2\rangle\ |\chi_3\rangle \cdots |\chi_N\rangle)\ \underline{\underline{C}}$$

$$\underline{\underline{H}}_{\text{m.o.}} = \underline{\underline{\tilde{C}}}^* \underline{\underline{H}}_{\text{a.o.}} \underline{\underline{C}}$$

$$\underline{\underline{H}}_{\text{m.o.}} = \underline{\underline{E}}$$ (*kinda neat!*)